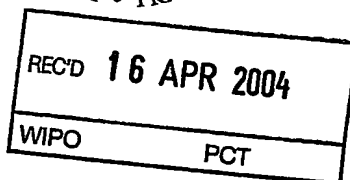




PC1/EP200 4 / 002255



INVESTOR IN PEOPLE



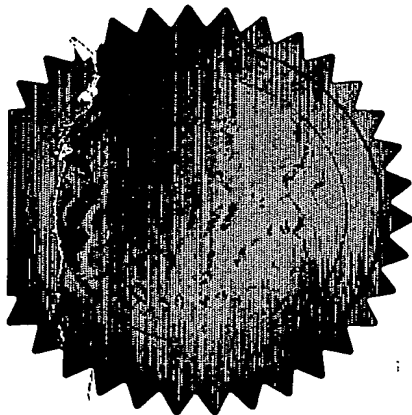
The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed

Dated 10 February 2004

**PRIORITY
DOCUMENT**

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

An Executive Agency of the Department of Trade and Industry

1/77

EUROPEAN PATENT OFFICE

Patents Form 1/77

Patents Act 1977
(Rule 16)THE PATENT OFFICE
RN

- 7 APR 2003

The
Patent
Office

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form.)

The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH

1. Your reference

MBZ-0521

2. Patent application number

(The Patent Office will fill in this part)

0307948.0

3. Full name, address and postcode of the or of each applicant (underline all surnames)

MBT Holding AG
Vulkanstrasse 110
CH-8048 Zürich
Switzerland

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

7171101001
Switzerland

4. Title of the invention

COMPOSITION

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Mr. P. Brown
FEE MBT
Albany House
Swinton Hall Road
Swinton
MANCHESTER M27 4DT

Patents ADP number (if you know it)

7178570001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country	Priority application number (if you know it)	Date of filing (day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if)

- a) any applicant named in part 3 is not an inventor, or
 b) there is an inventor who is not named as an applicant, or
 c) any named applicant is a corporate body.
 See note (d))

Yes

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document.

Continuation sheets of this form

Description

R

Claims

Abstract

1

Drawing(s)

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right
to grant of a patent (Patents Form 1770)

**Request for preliminary examination
and search (Form 9/77)**

Request for substantive examination
(Patent Form 10/77)

Any other documents
(please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature

Date _____

07.04.2003

12. Name and daytime telephone number of person to contact in the United Kingdom

Mr. P. Brown, FEB MBT
(0161) 794 7411

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act, 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- a) If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- b) Write your answers in capital letters using black ink or you may type them.
- c) If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- d) If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- e) Once you have filled in the form you must remember to sign and date it.
- f) For details of the fee and ways to pay please contact the Patent Office.

COMPOSITION

This invention relates to chemical compositions which bring about improvements in the properties of cementitious compositions.

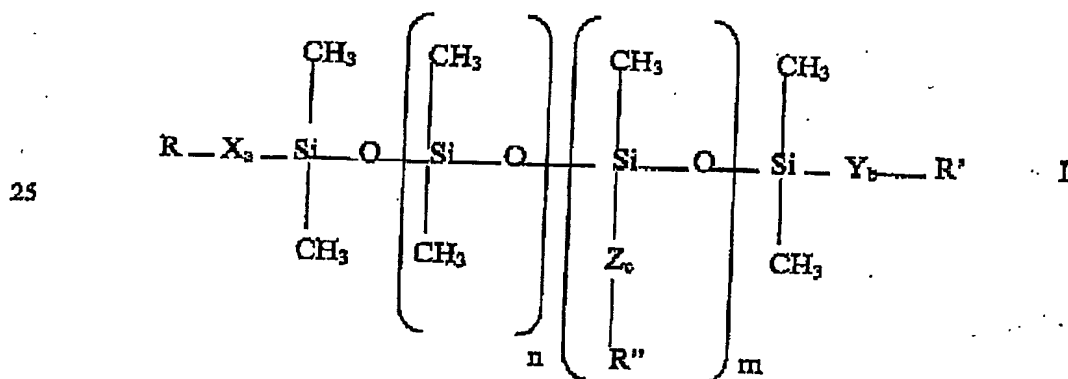
5

The chemical composition comprises a fluid blend of

- (i) at least one polyalkylene oxide, the alkylene oxide units being ethylene and propylene oxides;
- 10 (ii) at least one aqueous paraffin emulsion; and
- (iii) at least one siloxane compound that is at least one of liquid and soluble in at least one of water and aqueous alkali.

By "siloxane compound" is meant any siloxane-based material, that is, a material having
15 a linear or branched siloxane backbone chain of the form $-\text{SiR}^a\text{R}^b-\text{O}-\text{SiR}^c\text{R}^d-\text{O}-$. Any such material will work in this invention, provided that it is liquid or at least slightly soluble in at least one of water and aqueous alkali.

Preferred siloxane compounds for use in this invention are selected from those that
20 correspond to the general formula I



30 where m and n are independently from 1-2000, preferably from 1-500 and more preferably from 1-200, a, b, and c are independently either 0 or 1 and X, Y and Z are selected from

-O-;

-O-(CH₂)₁₋₃₀-, this moiety being at least one of linear, branched and containing at least one ring;

5 -(CH₂)₁₋₃₀-, this moiety being at least one of linear, branched and containing at least one ring;

-CH₂-CH₂-CH₂-O-;

-CH₂-CH₂-CH₂-O-CH₂-CHOH-CH₂-;

-CH₂-CH₂-CH₂-O-CH₂-CHOH-CH₂-O-;

-CH₂-CH₂-CH₂-O-CH₂-CHOH-CH₂-N-;

10

and R, R' and R'' are independently selected from at least one of hydrogen, C₁₋₁₀₀ alkyl, C₆₋₃₀ aryl, C₇₋₃₀ aralkyl; C₇₋₃₀ alkaryl; C₁₋₃₀ hydroxyalkyl; C₃₋₂₀₀ polyhydroxyalkyl; polyether consisting of from 2-200 identical or different C₁₋₁₅ oxyalkylene units; C₁₋₃₀ aminoalkyl; polyiminopolyalkylene having from 1-20 identical or different C₂₋₁₅ alkylene units; polyiminopolyoxyalkylene having from 1-20 identical or different C₂₋₁₅ oxyalkylene units; C₃₋₃₀ quaternary ammonium, optionally completely or partially ionised with at least one anion; C₄₋₃₀ betaine; carboxyl, optionally completely or partially ionised with any suitable cation; C₄₋₃₀ polycarboxyalkyl, optionally completely or partially ionised with at least one cation; sulpho group, optionally completely or partially ionised with at least one cation; thiosulpho group, optionally completely or partially ionised with at least one cation; epoxide group; glycidyl; acrylate; C₁₋₃₀ ester; polyester consisting of from 2-200 C₂₋₁₅ diacid and diester monomer units; and esters of inorganic acids, all alkyl chains being at least one of linear, branched and comprising at least one ring.

20

25 A more preferred class of siloxane compounds comprises those of Formula I in which a, b, and c are all 1 and X, Y and Z are selected from

-O-(CH₂)₁₋₃₀-, this moiety being linear or branched;

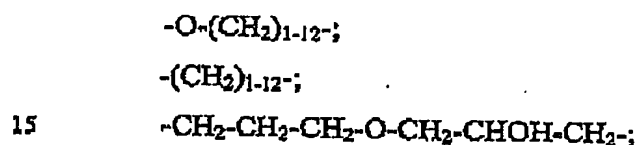
30 -(CH₂)₁₋₃₀-, this moiety being linear or branched;

-CH₂-CH₂-CH₂-O-CH₂-CHOH-CH₂-;

and R, R' and R'' are independently selected from at least one of hydrogen; hydroxy; polyether consisting of from 2-200 identical or different C₂₋₆ oxyalkylene units, with the

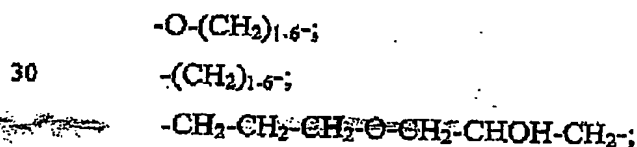
proviso that, if there is present more than one type of oxyalkylene unit, there shall be present at least two of each unit; C₃₋₃₀ quaternary ammonium, optionally completely or partially ionised with at least one anion; C₄₋₃₀ betaine; carboxyl, optionally completely or partially ionised with at least one cation; sulpho group, optionally completely or partially ionised with at least one cation; thiosulpho group, optionally completely or partially ionised with at least one cation; glycidyl; and acrylate; all alkyl chains being at least one of linear, branched and comprising at least one ring.

An even more preferred class of siloxane compounds comprises those of Formula I in which m and n are independently selected from 1-200, a, b, and c are all 1 and X, Y and Z are selected from



and R, R' and R'' are independently selected from at least one of hydrogen; hydroxy; polyether consisting of from 2-200 identical or different C₂₋₆ oxyalkylene units, with the proviso that, if there is present more than one type of oxyalkylene unit, there shall be present at least two of each unit; C₃₋₃₀ quaternary ammonium, optionally completely or partially ionised with at least one anion; C₄₋₃₀ betaine; carboxyl, optionally completely or partially ionised with at least one cation; glycidyl; and acrylate; all alkyl chains being capable of being linear or branched.

An even more preferred class of siloxane compounds comprises those of Formula I in which m is from 1-30 and n is from 1-100, a, b, and c are all 1 and X, Y and Z are selected from



and R, R' and R'' are independently selected from at least one of hydrogen; hydroxy; polyether consisting of from 2-200 identical or different C₂₋₆ oxyalkylene units, with the proviso that, if there is present more than one type of oxyalkylene unit, there shall be present at least two of each unit; C₃₋₂₀ quaternary ammonium, optionally completely or partially ionised with at least one anion; C₄₋₁₀ betaine and carboxyl, optionally completely or partially ionised with at least one cation; all alkyl chains being capable of being linear or branched.

The siloxanes hereinabove described may be any such material known to the art. Such materials are well known to the art for a variety of purposes, one of these being as antifoams in various industries. The preferred materials are those where R and R' are methyl or ethyl, n is from 5-200, more preferably from 10-150 and most preferably from 40-100, and m is from 1-100, more preferably from 2-40 and most preferably from 5-10.

The two different types of siloxane units may be arranged randomly or in blocks on the molecule. It is possible to utilise more than one type of moiety R''. Examples of R'' include ethylene oxide - propylene oxide copolymers of from 10 to 100 units.

The siloxanes that are useful in the present invention may either be incorporated into a dry cementitious composition, or they may be added to such a composition when it is mixed with water immediately prior to placement. The quantity required depends on the type of cement and the precise nature of the siloxane, but a typical range of weight proportions is from 0.05%-20% by weight of the weight of the cement, more preferably from 0.1-5%, even more preferably from 0.1-2% and most preferably from 0.2-1%.

In a further embodiment of the invention, the siloxane may be used in conjunction with hydrophobic, finely-divided silica. This can be added to the composition separately from the siloxane, but it is preferred that it be incorporated into the siloxane by, for example, blending or mixing. The quantity of silica can be up to 20% by weight of the siloxane, preferably no more than 10%. In a yet further embodiment of the invention, the siloxane may additionally contain emulsifier. Any suitable emulsifiers may be used in art-recognised quantities. Some commercially-available emulsifiers already contain emulsifier, so addition may be unnecessary.

Preferably the polyalkylene oxide is polyethylene oxide. The weight-average molecular weight is from 100,000-8,000,000, preferably from 2,000,000-5,000,000.

There are many types of paraffin emulsions available and any of these may be used in the working of the invention. By "paraffin emulsion" is meant an aqueous emulsion of a higher alkane having a fusion point above ambient temperature, which upon drying of the emulsion does not form a film in the sense that a paint forms a film (see also Römpp "Chemie Lexikon", 9th edition (Thieme Verlag 1989), volume 1, page 102, the contents of which are incorporated herein by reference). The emulsion may be stabilised by any convenient means, but it is preferable to use an ionically-emulsified (preferably anionically-stabilised) paraffin mixture (fusion point of 45-51°C) with a particle size of less than 2µM. Examples of such paraffin emulsions are "Mobilcer" 55 or "Mulrex" 62 from Mobil and "Ubatol" FPG 860 from Cray Valley and "Tecol" BC 60/40 from Trüb Emulsion Chemie.

The concentrations of the three ingredients and water in the chemical composition are shown below (as percentages by weight of the total composition). In some cases, the blend of the three ingredients is sufficiently fluid to make any water unnecessary, but generally some water is necessary, sometimes in relatively high proportion (when, for example, the polyethylene oxide is of high molecular weight).

	<u>Widest limits</u>	<u>preferred</u>	<u>more preferred</u>
siloxane	5-60	10-50	20-40
paraffin wax	10-70	20-60	30-50
polyethylene oxide	0.1-5	0.2-2	0.5-1.5
water	0-80	20-70	30-50

The three materials may be mixed into a dry cement, mortar or concrete mix, to which water need only be added, or they may be added individually or collectively in any combination to a cementitious mix when water is being added, prior to final use. It is preferred to combine the three (with water if necessary) in a single admixture. The material has a long shelf life and is ready for use without any prior preparation.

In use, the chemical composition is added in a quantity of from 0.01 – 100% by weight on cement. The water content may be varied over wide limits, depending on the effect desired. It is preferred to have relatively little water content, i.e., preferably less than 50% by weight of the composition. In such a case, the preferred quantity by weight on cement
5 is from 0.05-10%, more preferably from 0.1-3% and most preferably from 0.2-2%.

The use of the composition has a considerable and highly beneficial effect on any cementitious composition in which it is incorporated. Not only is the shrinkage and cracking decreased or even eliminated, as hereinabove described, but there may also be
10 noticeable improvements in properties such as freeze-thaw resistance and permeability, and there can also be a significant plasticising effect. The nature and extent of improvement will depend on the type of cementitious mix and the natures and concentrations of the various constituent raw materials, but there is always some enhancement. The invention therefore also provides a method of modifying the properties
15 of a cementitious composition, comprising adding to a fluid cementitious mix a chemical composition as hereinabove described. The invention further provides a cementitious composition having improved properties, which composition comprises a chemical composition as hereinabove described.

20 In addition to the one or three materials hereinabove described, there can also be added to the cementitious mix materials known to the art for the performance of particular functions, in art-recognised quantities. Such materials include (but are not limited to) plasticisers and superplasticisers, accelerators, antifreeze agents, pigments, air-entraining agents, retarders and reinforcing fibres of metal, glass or polymer.

25

The invention is further described with reference to the following non-limiting examples.

A number of materials are tested in a standard concrete mix, the mix design being as follows:

30

Cement	450	kg/m ³
Aggregate		
0-4 mm	990	kg/m ³
4-8 mm	660	kg/m ³

Water-to-cement ratio = 0.47

The materials tested are as follows:

5

Admixture 1 - a blend of a commercial paraffin wax emulsion ("Tecol" BC 60/40 from Trüb Emulsion Chemie) and a polyethylene oxide of MW 4,000,000 ("Polyox" (trade mark) 301 from Union Carbide), the blend containing 40% by weight paraffin emulsion and 1% polyethylene oxide

10 Admixture 2 - Admixture 1 + siloxane (a polyether siloxane wherein $m+n=75$, having on average per molecule 6.5 ethylene oxide/propylene oxide side chains of MW 1800)

Admixture 3 - a commercial neopentyl glycol-based shrinkage reducing agent.

15 Admixture 4 - a commercial shrinkage-reducing agent which is a blend of polyoxyalkylene ethers.

In all cases, 1% admixture by weight of cement is used, except in the case of Admixture 2, where 1% each of Admixture 1 and siloxane are used.

20 The drying free shrinkage is measured by German Standard Test Method DIN 52 450. The results are shown in the following table:

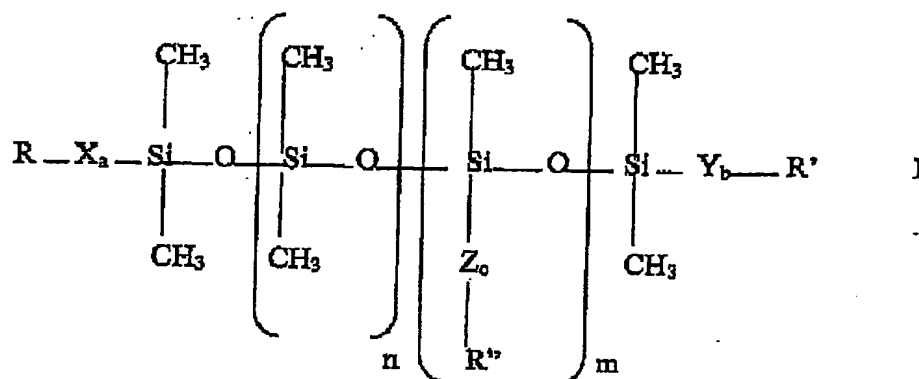
Drying free shrinkage (mm/m)					
Age (days)	No admixture	Admixture 1	Admixture 2	Admixture 3	Admixture 4
1	0	0	0	0	0
3	0.068	0.077	-0.044	0.026	-0.011
7	0.173	0.177	-0.004	0.129	0.046
14	0.235	0.228	0.028	0.203	0.127
21	0.283	0.294	0.066	0.234	0.157
28	0.328	0.329	0.102	0.272	0.213
38	0.365	0.359	0.121	0.282	0.223
58	0.416	0.423	0.193	0.35	0.261
67	0.433	0.428	0.233	0.387	
87	0.473	0.485	0.271	0.389	0.341

100

1. A composition for improving the properties of a cementitious composition, comprising a fluid blend of

- (i) at least one polyalkylene oxide, the alkylene oxide units being ethylene and propylene oxides;
- (ii) at least one aqueous paraffin emulsion; and
- (iii) at least one siloxane compound that is at least one of liquid and soluble in at least one of water and aqueous alkali.

2. A composition according to claim 1, in which the siloxane is selected from those that correspond to the general formula I:



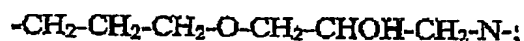
where m and n are independently from 1-2000, preferably from 1-500 and more preferably from 1-200, a, b, and c are independently either 0 or 1 and X, Y and Z are selected from

-0-

-O-(CH₂)₁₋₃₀, this moiety being at least one of linear, branched and containing at least one ring;

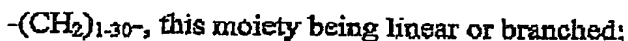
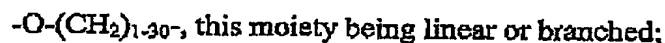
-(CH₂)₁₋₃₀, this moiety being at least one of linear, branched and containing at least one ring;

$$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-;$$
$$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CHOH}-\text{CH}_2-$$



and R, R' and R'' are independently selected from at least one of hydrogen, C₁₋₁₀₀ alkyl, C₆₋₃₀ aryl, C₇₋₃₀ aralkyl; C₇₋₃₀ alkaryl; C₁₋₃₀ hydroxyalkyl; C₃₋₂₀₀ polyhydroxyalkyl; polyether consisting of from 2-200 identical or different C₁₋₁₅ oxyalkylene units; C₁₋₃₀ aminoalkyl; polyiminopolyalkylene having from 1-20 identical or different C₂₋₁₅ alkylene units; polyiminopolyoxyalkylene having from 1-20 identical or different C₂₋₁₅ oxyalkylene units; C₃₋₃₀ quaternary ammonium, optionally completely or partially ionised with at least one anion; C₄₋₃₀ betaine; carboxyl, optionally completely or partially ionised with any suitable cation; C₄₋₃₀ polycarboxyalkyl, optionally completely or partially ionised with at least one cation; sulpho group, optionally completely or partially ionised with at least one cation; thiosulpho group, optionally completely or partially ionised with at least one cation; epoxide group; glycidyl; acrylate; C₁₋₃₀ ester; polyester consisting of from 2-200 C₂₋₁₅ diacid and diester monomer units; and esters of inorganic acids, all alkyl chains being at least one of linear, branched and comprising at least one ring.

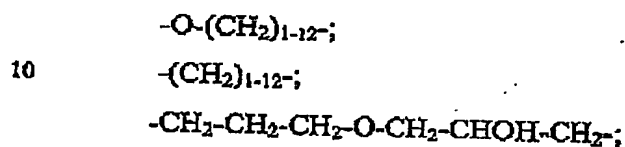
3. A composition according to claim 1 or claim 2, in which the siloxane is selected from those of Formula I in which a, b, and c are all 1 and X, Y and Z are selected from



and R, R' and R'' are independently selected from at least one of hydrogen; hydroxy; polyether consisting of from 2-200 identical or different C₂₋₆ oxyalkylene units, with the proviso that, if there is present more than one type of oxyalkylene unit, there shall be present at least two of each unit; C₃₋₃₀ quaternary ammonium, optionally completely or partially ionised with at least one anion; C₄₋₃₀ betaine; carboxyl, optionally completely or partially ionised with at least one cation; sulpho group, optionally completely or partially ionised with at least one cation; thiosulpho

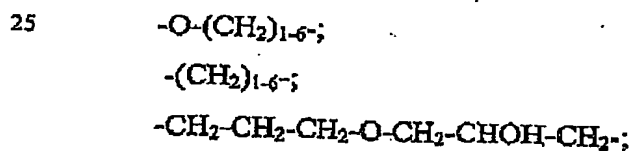
group, optionally completely or partially ionised with at least one cation; glycidyl; and acrylate; all alkyl chains being at least one of linear, branched and comprising at least one ring.

- 5 4. A composition according to any one of claims 1-3, in which the siloxane is selected from those of Formula I in which m and n are independently selected from 1-200, a, b, and c are all 1 and X, Y and Z are selected from



15 and R, R' and R'' are independently selected from at least one of hydrogen; hydroxy; polyether consisting of from 2-200 identical or different C_{2-6} oxyalkylene units, with the proviso that, if there is present more than one type of oxyalkylene unit, there shall be present at least two of each unit; C_{3-30} quaternary ammonium, optionally completely or partially ionised with at least one anion; C_{4-30} betaine; carboxyl, optionally completely or partially ionised with at least one cation; glycidyl; and acrylate; all alkyl chains being capable of being linear or branched.

- 20 5. A composition according to any one of claims 1-4, in which the siloxane is selected from those of Formula I in which m is from 1-30 and n is from 1-100, a, b, and c are all 1 and X, Y and Z are selected from



30 and R, R' and R'' are independently selected from at least one of hydrogen; hydroxy; polyether consisting of from 2-200 identical or different C_{2-6} oxyalkylene units, with the proviso that, if there is present more than one type of oxyalkylene unit, there shall be present at least two of each unit; C_{3-30} quaternary ammonium, optionally completely or partially ionised with at least one anion; C_{4-10} betaine and

carboxyl, optionally completely or partially ionised with at least one cation; all alkyl chains being capable of being linear or branched.

6. A composition according to any one of claims 1-5 in which the polyalkylene oxide
5 is polyethylene oxide.
7. A composition according to any one of claims 1-6 in which the weight-average molecular weight of the polyalkylene oxide is 100,000-8,000,000, preferably 2,000,000-5,000,000.
10
8. A composition according to any one of claims 1-7 in which the paraffin emulsion is an ionically-emulsified paraffin mixture with a fusion point of 45-51°C and a particle size of less than 2µM.
- 15 9. A method of modifying the properties of a cementitious composition, comprising adding to a fluid cementitious mix a composition according to any one of claims 1-8.
10. A cementitious mix having improved properties, which composition comprises a
20 chemical composition according to claims 1-8.

ABSTRACT

A composition for improving the properties of a cementitious composition comprises a fluid blend of at least one polyalkylene oxide, at least one aqueous paraffin emulsion, at
5 least one siloxane and, if necessary for fluidity, water.

PCT/EP2004/002255

